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<p>(54) Title: METAL COMPLEXES FOR USE AS GAS GENERANTS</p> <p>(57) Abstract</p> <p>Gas generating compositions and methods for their use are provided. Metal complexes are used as gas generating compositions. These complexes are comprised of a cationic metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen. The complexes are formulated such that when the complex combusts nitrogen gas and water vapor is produced. Specific examples of such complexes include metal nitrite ammine, metal nitrate ammine, and metal perchlorate ammine complexes, as well as hydrazine complexes. Such complexes are adaptable for use in gas generating devices such as automobile air bags.</p>		

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METAL COMPLEXES FOR USE AS GAS GENERANTS

Field of the Invention

5 The present invention relates to complexes or transition metals or alkaline earth metals which are capable of combusting to generate gases. More particularly, the present invention relates to providing such complexes which rapidly oxidize to produce significant quantities of gases, particularly water vapor and nitrogen.

Background of the Invention

10 Gas generating chemical compositions are useful in a number of different contexts. One important use for such compositions is in the operation of "air bags." Air bags are gaining in acceptance to the point that many, if not most, new automobiles are equipped with such devices. Indeed, many new automobiles are equipped with multiple air bags to protect the driver and passengers.

20 In the context of automobile air bags, sufficient gas must be generated to inflate the device within a fraction of a second. Between the time the car is impacted in an accident, and the time the driver would otherwise be thrust against the steering wheel, the air bag must fully inflate. As a consequence, nearly instantaneous gas generation is required.

25 There are a number of additional important design criteria that must be satisfied. Automobile manufacturers and others have set forth the required criteria which must be met in detailed specifications. Preparing gas generating compositions that meet these important design criteria is an extremely difficult task. These specifications require that the gas generating composition produce gas at a required rate. The specifications also place strict limits on the generation of toxic or harmful gases or solids. Examples of restricted gases include carbon monoxide, carbon dioxide, NO_x, SO_x, and hydrogen sulfide.

35 The gas must be generated at a sufficiently and reasonably low temperature so that an occupant of the car is not burned

upon impacting an inflated air bag. If the gas produced is overly hot, there is a possibility that the occupant of the motor vehicle may be burned upon impacting a just deployed air bag. Accordingly, it is necessary that the combination of the gas generant and the construction of the air bag isolates automobile occupants from excessive heat. All of this is required while the gas generant maintains an adequate burn rate.

Another related but important design criteria is that the gas generant composition produces a limited quantity of particulate materials. Particulate materials can interfere with the operation of the supplemental restraint system, present an inhalation hazard, irritate the skin and eyes, or constitute a hazardous solid waste that must be dealt with after the operation of the safety device. In the absence of an acceptable alternative, the production of irritating particulates is one of the undesirable, but tolerated aspects of the currently used sodium azide materials.

In addition to producing limited, if any, quantities of particulates, it is desired that at least the bulk of any such particulates be easily filterable. For instance, it is desirable that the composition produce a filterable slag. If the reaction products form a filterable material, the products can be filtered and prevented from escaping into the surrounding environment. This also limits interference with the gas generating apparatus and the spreading of potentially harmful dust in the vicinity of the spent air bag which can cause lung, mucous membrane and eye irritation to vehicle occupants and rescuers.

Both organic and inorganic materials have been proposed as possible gas generants. Such gas generant compositions include oxidizers and fuels which react at sufficiently high rates to produce large quantities of gas in a fraction of a second.

At present, sodium azide is the most widely used and currently accepted gas generating material. Sodium azide nominally meets industry specifications and guidelines. Nevertheless, sodium azide presents a number of persistent

problems. Sodium azide is relatively toxic as a starting material, since its toxicity level as measured by oral rat LD₅₀ is in the range of 45 mg/kg. Workers who regularly handle sodium azide have experienced various health problems such as severe headaches, shortness of breath, convulsions, and other symptoms.

In addition, no matter what auxiliary oxidizer is employed, the combustion products from a sodium azide gas generant include caustic reaction products such as sodium oxide, or sodium hydroxide. Molybdenum disulfide or sulfur have been used as oxidizers for sodium azide. However, use of such oxidizers results in toxic products such as hydrogen sulfide gas and corrosive materials such as sodium oxide and sodium sulfide. Rescue workers and automobile occupants have complained about both the hydrogen sulfide gas and the corrosive powder produced by the operation of sodium azide-based gas generants.

Increasing problems are also anticipated in relation to disposal of unused gas-inflated supplemental restraint systems, e.g. automobile air bags, in demolished cars. The sodium azide remaining in such supplemental restraint systems can leach out of the demolished car to become a water pollutant or toxic waste. Indeed, some have expressed concern that sodium azide might form explosive heavy metal azides or hydrazoic acid when contacted with battery acids following disposal.

Sodium azide-based gas generants are most commonly used for air bag inflation, but with the significant disadvantages of such compositions many alternative gas generant compositions have been proposed to replace sodium azide. Most of the proposed sodium azide replacements, however, fail to deal adequately with all of the criteria set forth above.

It will be appreciated, therefore, that there are a number of important criteria for selecting gas generating compositions for use in automobile supplemental restraint systems. For example, it is important to select starting materials that are not toxic. At the same time, the combustion products must not be toxic or harmful. In this regard, industry standards limit

the allowable amounts of various gases produced by the operation of supplemental restraint systems.

It would, therefore, be a significant advance to provide compositions capable of generating large quantities of gas that would overcome the problems identified in the existing art. It would be a further advance to provide a gas generating composition which is based on substantially nontoxic starting materials and which produces substantially nontoxic reaction products. It would be another advance in the art to provide a gas generating composition which produces very limited amounts of toxic or irritating particulate debris and limited undesirable gaseous products. It would also be an advance to provide a gas generating composition which forms a readily filterable solid slag upon reaction.

Such compositions and methods for their use are disclosed and claimed herein.

Summary and Objects of the Invention

The present invention is related to the use of complexes of transition metals or alkaline earth metals as gas generating compositions. These complexes are comprised of a cationic metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen. In some cases the oxidizing anion is coordinated with the metal template. The complexes are formulated such that when the complex combusts nitrogen gas and water vapor is produced. Importantly, the production of other undesirable gases is substantially eliminated.

Specific examples of such complexes include metal nitrite ammine, metal nitrate ammine, metal perchlorate ammine, and metal hydrazine complexes. The complexes within the scope of the present invention rapidly combust or decompose to produce significant quantities of gas.

The metals incorporated within the complexes are transition metals or alkaline earth metals that are capable of forming ammine or hydrazine complexes. The presently preferred metal is cobalt. Other metals which also form complexes with

the properties desired in the present invention include, for example, magnesium, manganese, nickel, vanadium, copper, chromium, and zinc. Examples of other usable metals include rhodium, iridium, ruthenium, palladium, and platinum. These metals are not as preferred as the metals mentioned above, primarily because of cost considerations.

The transition metal or alkaline earth metal acts as a template at the center of a nitrite ammine, nitrate ammine, perchlorate ammine, or hydrazine complex. An ammine complex is generally defined as a coordination complex including ammonia, whereas a hydrazine complex is similarly defined as a coordination complex containing hydrazine. Thus, examples of metal complexes within the scope of the present invention include $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ (tetraamminecopper(II) nitrate), $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$ (trinitrotriamminecobalt (III)), $\text{Co}(\text{NH}_3)_6(\text{ClO}_4)_3$ (hexaammine cobalt (III) perchlorate), $\text{Zn}(\text{N}_2\text{H}_4)_3(\text{NO}_3)_2$ (tris-hydrazine zinc nitrate), $\text{Mg}(\text{N}_2\text{H}_4)_2(\text{ClO}_4)_2$ (bis-hydrazine magnesium perchlorate), and $\text{Pt}(\text{NO}_2)_2(\text{NH}_2\text{NH}_2)_2$ (bis-hydrazine platinum (II) nitrite).

It is observed that transition metal complexes of this type combust rapidly to produce significant quantities of gases. Combustion can be initiated by the application of heat or by the use of conventional igniter devices.

Some of the complexes of the present invention combust stoichiometrically to a metal or metal oxide, nitrogen and water. That is, it is not necessary to allow the complex to react with any other material in order to produce gas. In other cases, however, it is desirable to add a further oxidizing agent or fuel in order to accomplish efficient combustion and gas production. These materials are added in oxidizing or fuel effective quantities as needed.

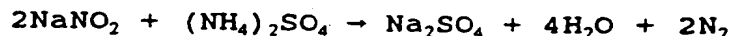
Detailed Description of the Invention

As discussed above, the present invention is related to the use of complexes or transition metals or alkaline earth metals as gas generating compositions. These complexes are comprised of a cationic metal template, sufficient oxidizing

anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen. In some cases the oxidizing anion is coordinated with the metal template. The complexes are formulated such that when the complex combusts, nitrogen gas and water vapor is produced. The combustion takes place at a rate sufficient to qualify such materials for use as gas generating compositions in automobile air bags and other similar types of devices. Importantly, the production of other undesirable gases is substantially eliminated.

Complexes which fall within the scope of the present invention include metal nitrate amines, metal nitrite amines, metal perchlorate amines, and metal hydrazines. As mentioned above, ammine complexes are defined as coordination complexes including ammonia. Thus, the present invention relates to ammine complexes which also include one or more nitrite (NO_2) or nitrate (NO_3) groups in the complex. In certain instances, the complexes may include both nitrite and nitrate groups in a single complex. The present invention also relates to similar perchlorate ammine complexes, and metal complexes containing one or more hydrazine groups and corresponding oxidizing anions.

It is suggested that during combustion of a complex containing nitrite and ammonia groups, the nitrite and ammonia groups undergo a diazotization reaction. This reaction is similar, for example, to the reaction of sodium nitrite and ammonium sulfate, which is set forth as follows:



Compositions such as sodium nitrite and ammonium sulfate in combination have little utility as gas generating substances. These materials are observed to undergo metathesis reactions which result in unstable ammonium nitrite. In addition, most simple nitrite salts have limited stability.

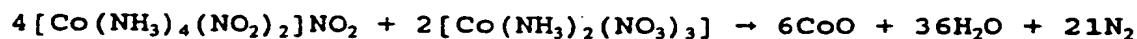
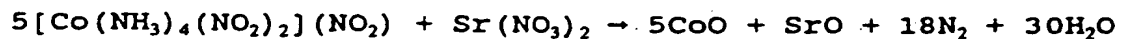
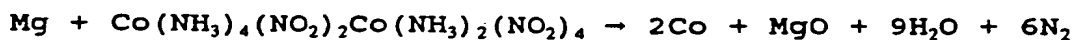
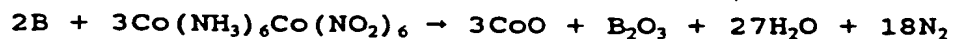
In contrast, the metal complexes of the present invention provide stable materials which are, in certain instances, still capable of undergoing the type of reaction set forth above.

The complexes of the present invention also produce reaction products which include desirable quantities of non toxic gases such as water vapor and nitrogen. In addition, a stable metal, or metal oxide slag is formed. Thus, the compositions of the present invention avoid several of the limitations of existing sodium azide gas generating compositions.

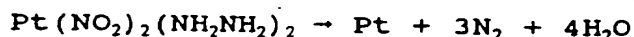
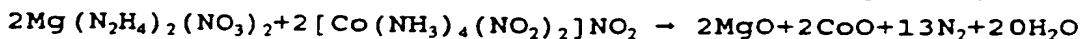
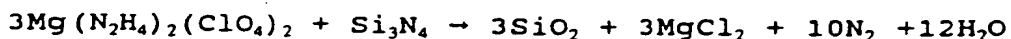
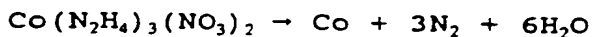
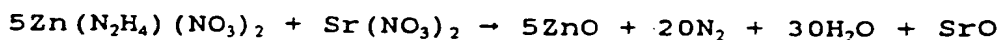
Any transition metal or alkaline earth metal which is capable of forming the complexes described herein is a potential candidate for use in these gas generating compositions. However, considerations such as cost, thermal stability, and toxicity may limit the most preferred group of metals.

The presently preferred metal is cobalt. Cobalt forms stable complexes which are relatively inexpensive. In addition, the reaction products of cobalt complex combustion are relatively non-toxic. Other preferred metals include magnesium, manganese, copper, and zinc. Examples of less preferred but usable metals include nickel, vanadium, chromium, rhodium, iridium, ruthenium, and platinum.

Examples of ammine complexes within the scope of the present invention, and the associated gas generating decomposition reactions are as follows:



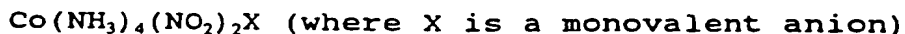
Examples of hydrazine complexes within the scope of the present invention, and related gas generating reactions are as follows:



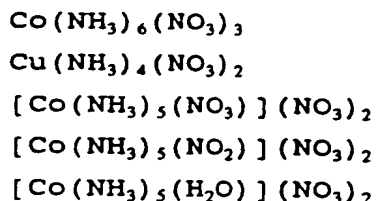
While the complexes of the present invention are relatively stable, it is also simple to initiate the combustion reaction. For example, if the complexes are contacted with a hot wire, rapid gas producing combustion reactions are observed. Similarly, it is possible to initiate the reaction by means of conventional igniter devices. One type of igniter device includes a quantity of BKNO_3 pellets which is ignited, and which in turn is capable of igniting the compositions of the present invention.

It is also of importance to note that many of the complexes defined above undergo "stoichiometric" decomposition. That is, the complexes decompose without reacting with any other material to produce large quantities of gas, and a metal or metal oxide. However, for certain complexes it may be desirable to add a fuel or oxidizer to the complex in order to assure complete and efficient reaction. Such fuels include, for example, boron, magnesium, aluminum, hydrides of boron or aluminum, silicon, titanium, zirconium, and other similar convention fuel materials. Oxidizing species include nitrates, nitrites, chlorates, perchlorates, peroxides, and other similar oxidizing materials. Thus, while stoichiometric decomposition is attractive because of the simplicity of the composition and reaction, it is also possible to use complexes for which stoichiometric decomposition is not possible.

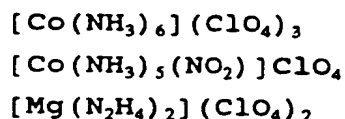
Examples of non-stoichiometric complexes include:



As mentioned above, nitrate and perchlorate complexes also fall within the scope of the invention. Examples of such nitrate complexes include:



Examples of perchlorate complexes within the scope of the invention include:



Preparation of metal nitrite or nitrate ammine complexes of the present invention is described in the literature. Specifically, reference is made to Hagel, "The Triamines of Cobalt (III). I. Geometrical Isomers of Trinitrotriamminecobalt(III)," 9 Inorganic Chemistry 1496 (June 1970); Shibata, et al. "Synthesis of Nitroammine- and Cyanoamminecobalt(III) Complexes With Potassium Tricarbonatocobaltate(III) as the Starting Material," 3 Inorganic Chemistry 1573 (Nov. 1964); Wieghardt, "mu. -Carboxylatodi-.mu.-hydroxo-bis[triamminecobalt(III)] Complexes," 23 Inorganic Synthesis 23 (1985); Laing, "Mer- and fac-triamminetrinitrocobalt(III): Do they exist?" 62 J. Chem Educ., 707 (1985); Siebert, "Isomers of Trinitrotriamminecobalt(III)," 441 Z. Anorg. Allg. Chem. 47 (1978); all of which are incorporated herein by this reference. Transition metal perchlorate ammine complexes are synthesized by similar methods. As mentioned above, the ammine complexes of the present invention are generally stable and safe for use in preparing gas generating formulations.

Preparation of metal perchlorate, nitrate, and nitrite hydrazine complexes is also described in the literature. Specific reference is made to Patil, et al. "Synthesis and Characterization of Metal Hydrazine Nitrate, Azide, and Perchlorate Complexes," 12 Synthesis and Reactivity In Inorganic and Metal Organic Chemistry, 383 (1982); Klyichnikov, et al. "Synthesis of Some Hydrazine Compounds of Palladium," 13 Zh. Neorg. Khim., 792 (1968); Ibid., "Conversion of Mononuclear Hydrazine Complexes of Platinum and Palladium Into Binuclear Complexes," 36 Ukr. Khim. Zh., 687 (1970).

The materials are also processible. The materials can be pressed into usable pellets for use in gas generating devices. Such devices include automobile air bag supplemental restraint systems. Such gas generating devices will comprise a quantity of the described complexes which can be defined generally as metal nitrite ammine, metal nitrate ammine, metal nitrite hydrazine, metal nitrate hydrazine, metal perchlorate ammine, and metal perchlorate hydrazine complexes wherein the metal is selected from the group consisting of transition metals. The complexes produce a mixture of gases, principally nitrogen and water vapor, by the decomposition of the complex. The gas generating device will also include means for initiating the decomposition of the composition, such as a hot wire or igniter. In the case of an automobile air bag system, the system will include the complexes described above; a collapsed, inflatable air bag; and means for igniting said gas-generating composition within the air bag system. Automobile air bag systems are well known in the art.

The gas generating compositions of the present invention are readily adapted for use with conventional hybrid air bag inflator technology. Hybrid inflator technology is based on heating a stored inert gas (argon or helium) to a desired temperature by burning a small amount of propellant. Hybrid inflators do not require cooling filters used with pyrotechnic inflators to cool combustion gases, because hybrid inflators are able to provide a lower temperature gas. The gas discharge temperature can be selectively changed by adjusting the ratio

of inert gas weight to propellant weight. The higher the gas weight to propellant weight ratio, the cooler the gas discharge temperature.

5 A hybrid gas generating system comprises a pressure tank having a rupturable opening, a pre-determined amount of inert gas disposed within that pressure tank; a gas generating device for producing hot combustion gases and having means for rupturing the rupturable opening; and means for igniting the gas generating composition. The tank has a rupturable opening
10 which can be broken by a piston when the gas generating device is ignited. The gas generating device is configured and positioned relative to the pressure tank so that hot combustion gases are mixed with and heat the inert gas. Suitable inert gases include, among others, argon, and helium and mixtures
15 thereof. The mixed and heated gases exit the pressure tank through the opening and ultimately exit the hybrid inflator and deploy an inflatable bag or balloon, such as an automobile air bag.

20 The high heat capacity of water vapor can be an added advantage for its use as a heating gas in a hybrid gas generating system. Thus, less water vapor, and consequently, less generant may be needed to heat a given quantity of inert gas to a given temperature. A preferred embodiment of the invention yields combustion products with a temperature in the
25 range of greater than about 1800°K, the heat of which is transferred to the cooler inert gas causing a further improvement in the efficiency of the hybrid gas generating system.

30 Hybrid gas generating devices for supplemental safety restraint application are described in Frantom, Hybrid Airbag Inflator Technology, Airbag Int'l Symposium on Sophisticated Car Occupant Safety Systems, (Weinbrenner-Saal, Germany, Nov. 2-3, 1992).

35 EXAMPLES

The present invention is further described in the following non-limiting examples. Unless otherwise stated, the

compositions are expressed in weight percent. As used herein, 1 pound equals 453.593 grams and 1 inch equals 0.0254 meters.

Example 1

5 A mixture of $2\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$ and $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4$ was prepared and pressed in a pellet having a diameter of approximately 0.504 inches. The complexes were prepared within the scope of the teachings of the Hagel, et al. reference identified above. The pellet was placed in a test bomb, which
10 was pressurized to 1,000 psi (pounds per square inch) with nitrogen gas.

The pellet was ignited with a hot wire and burn rate was measured and observed to be 0.38 inches per second. Theoretical calculations indicated a flame temperature of
15 1805°C . From theoretical calculations, it was predicted that the major reaction products would be solid CoO and gaseous reaction products. The major gaseous reaction products were predicted to be as follows:

20	<u>Product</u>	<u>Volume %</u>
	H_2O	57.9
	N_2	38.6
	O_2	3.1

Example 2

25 A quantity of $2\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$ was prepared according to the teachings of Example 1 and tested using differential scanning calorimetry. It was observed that the complex produced a vigorous exotherm at 200°C .

Example 3

Theoretical calculations were undertaken for $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$. Those calculations indicated a flame temperature of about $2,000^\circ\text{K}$ and a gas yield of about 1.75 times that of a
35 conventional sodium azide gas generating compositions based on equal volume of generating composition ("performance ratio").

Theoretical calculations were also undertaken for a series of gas generating compositions. The composition and the theoretical performance data is set forth below in Table I.

Table I

Gas Generant	Ratio	Temp. (C°)	Perf. Ratio
$\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$	-	1805	1.74
$\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$	-	1381	1.81
$\text{NH}_4[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]/\text{B}$	99/1	1634	1.72
$\text{Co}(\text{NH}_3)_6(\text{NO}_3)_3$	-	1585	2.19
$[\text{Co}(\text{NH}_3)_5(\text{NO}_3)](\text{NO}_3)_2$	-	1637	2.00
$[\text{Fe}(\text{N}_2\text{H}_4)_3](\text{NO}_3)_2/\text{Sr}(\text{NO}_3)_2$	87/13	2345	1.69
$[\text{Co}(\text{NO}_3)_6](\text{ClO}_4)_3/\text{CaH}_2$	86/14	2577	1.29
$[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$	-	1659	2.06

Performance ratio is a normalized relation to a unit volume of azide-based gas generant. The theoretical gas yield for a typical sodium azide-based gas generant (68 wt.% NaN_3 ; 30 wt% of MoS_2 ; 2 wt% of S) is about 0.85 g gas/cc NaN_3 generant.

Example 4

Theoretical calculations were conducted on the reaction of $[\text{Co}(\text{NO}_3)_6](\text{ClO}_4)_3$ and CaH_2 as listed in Table I to evaluate its use in a hybrid gas generator. If this formulation is allowed to undergo combustion in the presence of 6.80 times its weight in argon gas, the flame temperature decreases from 2577°C to 1085°C, assuming 100% efficient heat transfer. The output gases consist of 86.8% by volume argon, 1600 ppm (parts per million) by volume hydrogen chloride, 10.2% by volume water, and 2.9% by volume nitrogen. The total slag weight would be 6.1% by mass.

Summary

In summary the present invention provides gas generating materials that overcome some of the limitations of conventional azide-based gas generating compositions. The complexes of the

present invention produce non toxic gaseous products including water vapor, oxygen, and nitrogen. Certain of the complexes are also capable of stoichiometric decomposition to a metal or metal oxide, and nitrogen and water vapor. Accordingly, no other chemical species are required to drive the reaction. Finally, reaction temperatures and burn rates are within acceptable ranges.

The invention may be embodied in other specific forms without departing from its essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description.

CLAIMS:

1. A gas generating composition comprising a complex which comprises a cationic transition metal or alkaline earth metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen, such that when said complex combusts nitrogen gas and water vapor is produced.

2. A gas generating composition as defined in claim 1 wherein said anion is coordinated with the metal template.

3. A gas generating composition as defined in claim 1 wherein said complex is a metal nitrite ammine.

4. A gas generating composition as defined in claim 1 wherein said complex is a metal nitrate ammine.

5. A gas generating composition as defined in claim 1 wherein said complex is a metal perchlorate ammine.

6. A gas generating composition as defined in claim 1 wherein said complex is a metal hydrazine.

7. A gas generating composition as defined in claim 1 wherein the combustion of the complex is stoichiometric to a metal or metal oxide, water, and nitrogen.

8. A gas generating composition as defined in claim 1 wherein said mixture of gases comprises water vapor and nitrogen gas.

9. A gas generating composition as defined in claim 1 wherein said metal is cobalt.

10. A gas generating composition as defined in claim 1 wherein said metal is selected from the group consisting of magnesium, manganese, nickel, vanadium, copper, chromium, and zinc.

11. A gas generating composition as defined in claim 1 wherein said metal is selected from the group consisting of rhodium, iridium, ruthenium, palladium, and platinum.

12. A gas generating composition as defined in claim 1 wherein the combustion produces an excess of fuel and the composition further comprises an oxidizer-effective amount of an oxidizing agent.

13. A gas generating composition as defined in claim 12 wherein the oxidizing agent is selected from the group consisting of nitrates, nitrites, chlorates, perchlorates, peroxides, and metal oxides.

5 14. A gas generating composition as defined in claim 1 wherein the combustion produces an excess of oxidizing species and the composition further comprising a fuel-effective amount of a fuel.

10 15. A gas generating composition as defined in claim 14 wherein the fuel is selected from the group consisting of boron, aluminum, hydrides of boron or aluminum, silicon.

15 16. Gas generating compositions comprising a complex selected from the group consisting of metal nitrite ammines, metal nitrate ammines, metal perchlorate ammines, and metal hydrazines, wherein a mixture of gases comprising water vapor and nitrogen gas is produced by the combustion of the complex.

17. Gas generating compositions as defined in claim 16 wherein the combustion of the complex is stoichiometric to metal or metal oxide, nitrogen, and water vapor.

20 18. Gas generating compositions as defined in claim 16 wherein said mixture of gases comprises water vapor and nitrogen gas.

25 19. Gas generating compositions as defined in claim 16 wherein the mixture of gases is substantially free of carbon dioxide and carbon monoxide gases.

20. Gas generating compositions as defined in claim 16 wherein said metal is cobalt.

30 21. Gas generating compositions as defined in claim 16 wherein said metal is selected from the group consisting of magnesium, manganese, nickel, vanadium, copper, chromium, and zinc.

22. Gas generating compositions as defined in claim 16 wherein said metal is selected from the group consisting of rhodium, iridium, ruthenium, palladium, and platinum.

23. Gas generating compositions as defined in claim 16 wherein the combustion produces an excess of fuel and the composition further comprises an oxidizer-effective amount of an oxidizing agent.

5 24. Gas generating compositions as defined in claim 23 wherein the oxidizing agent is selected from the group consisting of nitrates, nitrites, chlorates, perchlorates, peroxides, and metal oxides.

10 25. Gas generating compositions as defined in claim 16 wherein the combustion produces an excess of oxidizing species and the composition further comprising a fuel-effective amount of a fuel.

15 26. Gas generating compositions as defined in claim 25 wherein the fuel is selected from the group consisting of boron, aluminum, hydrides of boron or aluminum, silicon.

20 27. A method of inflating an air bag comprising combusting a complex which comprises a cationic transition metal or alkaline earth metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen, such that when said complex combusts nitrogen gas and water vapor is produced.

25 28. A method of inflating an air bag as defined in claim 27 wherein the combustion of the complex is stoichiometric to a metal or metal oxide, nitrogen, and water.

29. A method of inflating an air bag as defined in claim 27 wherein the combustion of the metal complex is initiated by heat.

30 30. A method of inflating an air bag as defined in claim 27 wherein said mixture of gases comprises water vapor and nitrogen gas.

31. A method of inflating an air bag as defined in claim 27 wherein said mixture of gases is substantially free of carbon dioxide and carbon monoxide gases.

35 32. A method of inflating an air bag as defined in claim 27 wherein said metal is cobalt.

33. A method of inflating an air bag as defined in claim 27 wherein said metal is selected from the group consisting of magnesium, manganese, nickel, vanadium, copper, chromium, and zinc.

5 34. A method of inflating an air bag as defined in claim 27 wherein said metal is selected from the group consisting of rhodium, iridium, ruthenium, palladium, and platinum.

10 35. A method of inflating an air bag as defined in claim 27 wherein the combustion produces an excess of fuel and the composition further comprises an effective amount of an oxidizing agent.

15 36. A method of inflating an air bag as defined in claim 35 wherein the oxidizing agent is selected from the group consisting of nitrates, nitrites, chlorates, perchlorates, peroxides, and metal oxides.

37. A method of inflating an air bag as defined in claim 27 wherein the combustion produces an excess of fuel and the composition further comprises a fuel-effective amount of a fuel.

20 38. A method of inflating an air bag as defined in claim 37 wherein the fuel is selected from the group consisting of boron, aluminum, hydrides of boron or aluminum, silicon.

39. A method as defined in claim 27 wherein said anion is coordinated with the metal template.

25 40. A method as defined in claim 27 wherein said complex is a metal nitrite ammine.

41. A method as defined in claim 27 wherein said complex is a metal nitrate ammine.

30 42. A method as defined in claim 27 wherein said complex is a metal perchlorate ammine.

43. A method as defined in claim 27 wherein said complex is a metal hydrazine.

44. A gas generating device comprising:

a gas generating composition comprising a complex which comprises a cationic transition metal or alkaline earth metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen, such that when said complex combusts nitrogen gas and water vapor is produced; and

means for initiating the combustion of the composition.

45. An automobile air bag system comprising:

a collapsed, inflatable air bag;

a gas-generating device connected to said air bag for inflating said air bag, said gas-generating device containing a gas-generating composition comprising a complex which comprises a cationic transition metal or alkaline earth metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen, such that when said complex combusts nitrogen gas and water vapor is produced; and

means for igniting said gas-generating composition.

46. A vehicle containing a supplemental restraint system having an air bag system comprising:

a collapsed, inflatable air bag;

a gas-generating device connected to said air bag for inflating said air bag, said gas-generating device containing a gas-generating composition comprising a complex which comprises a cationic transition metal or alkaline earth metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen, such that when said complex combusts nitrogen gas and water vapor is produced; and

means for igniting said gas-generating composition.

47. A method of inflating an air bag comprising the step of combusting a complex selected from the group consisting of metal nitrite amines, metal nitrate amines, metal perchlorate amines, and metal hydrazines, wherein a mixture of gases comprising water vapor and nitrogen gas is produced by the combustion of the complex.

48. A method as defined in claim 47 wherein the combustion of the complex is stoichiometric to metal or metal oxide, nitrogen, and water vapor.

5 49. A method as defined in claim 47 wherein said mixture of gases comprises water vapor and nitrogen gas.

50. A method as defined in claim 47 wherein the mixture of gases is substantially free of carbon dioxide and carbon monoxide gases.

10

AMENDED CLAIMS

[received by the International Bureau on 07 June 1995 (07.06.95);
original claims 27,31-34,43 and 47 amended; new claims 51 and 52 added;
remaining claims unchanged (4 pages)]

23. Gas generating compositions as defined in claim 16 wherein the combustion produces an excess of fuel and the composition further comprises an oxidizer-effective amount of an oxidizing agent.

5 24. Gas generating compositions as defined in claim 23 wherein the oxidizing agent is selected from the group consisting of nitrates, nitrites, chlorates, perchlorates, peroxides, and metal oxides.

10 25. Gas generating compositions as defined in claim 16 wherein the combustion produces an excess of oxidizing species and the composition further comprising a fuel-effective amount of a fuel.

15 26. Gas generating compositions as defined in claim 25 wherein the fuel is selected from the group consisting of boron, aluminum, hydrides of boron or aluminum, silicon.

20 27. A method of inflating an air bag comprising combusting a complex which comprises a cationic transition metal or alkaline earth metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen, such that when said complex combusts, a mixture of gases comprising nitrogen gas and water vapor is produced.

25 28. A method of inflating an air bag as defined in claim 27 wherein the combustion of the complex is stoichiometric to a metal or metal oxide, nitrogen, and water.

29. A method of inflating an air bag as defined in claim 27 wherein the combustion of the metal complex is initiated by heat.

30 30. A method of inflating an air bag as defined in claim 27 wherein said mixture of gases comprises water vapor and nitrogen gas.

35 31. A method of inflating an air bag as defined in claim 27 wherein said inorganic oxidizing anion and said inorganic neutral ligand are substantially free of carbon and wherein said mixture of gases is substantially free of carbon dioxide and carbon monoxide gases.

32. A method of inflating an air bag as defined in claim 27 wherein said transition metal is cobalt.

33. A method of inflating an air bag as defined in claim 27 wherein said transition metal or alkaline earth metal is selected from the group consisting of magnesium, manganese, nickel, vanadium, copper, chromium, and zinc.

34. A method of inflating an air bag as defined in claim 27 wherein said transition metal is selected from the group consisting of rhodium, iridium, ruthenium, palladium, and platinum.

35. A method of inflating an air bag as defined in claim 27 wherein the combustion produces an excess of fuel and the composition further comprises an effective amount of an oxidizing agent.

36. A method of inflating an air bag as defined in claim 35 wherein the oxidizing agent is selected from the group consisting of nitrates, nitrites, chlorates, perchlorates, peroxides, and metal oxides.

37. A method of inflating an air bag as defined in claim 27 wherein the combustion produces an excess of fuel and the composition further comprises a fuel-effective amount of a fuel.

38. A method of inflating an air bag as defined in claim 37 wherein the fuel is selected from the group consisting of boron, aluminum, hydrides of boron or aluminum, silicon.

39. A method as defined in claim 27 wherein said anion is coordinated with the metal template.

40. A method as defined in claim 27 wherein said complex is a metal nitrite ammine.

41. A method as defined in claim 27 wherein said complex is a metal nitrate ammine.

42. A method as defined in claim 27 wherein said complex is a metal perchlorate ammine.

43. A method as defined in claim 27 wherein said complex is a metal nitrite hydrazine.

44. A gas generating device comprising:

a gas generating composition comprising a complex which comprises a cationic transition metal or alkaline earth metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen, such that when said complex combusts nitrogen gas and water vapor is produced; and

means for initiating the combustion of the composition.

45. An automobile air bag system comprising:

a collapsed, inflatable air bag;

a gas-generating device connected to said air bag for inflating said air bag, said gas-generating device containing a gas-generating composition comprising a complex which comprises a cationic transition metal or alkaline earth metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen, such that when said complex combusts nitrogen gas and water vapor is produced; and

means for igniting said gas-generating composition.

46. A vehicle containing a supplemental restraint system having an air bag system comprising:

a collapsed, inflatable air bag;

a gas-generating device connected to said air bag for inflating said air bag, said gas-generating device containing a gas-generating composition comprising a complex which comprises a cationic transition metal or alkaline earth metal template, sufficient oxidizing anion to balance the charge of the complex, and a neutral ligand containing hydrogen and nitrogen, such that when said complex combusts nitrogen gas and water vapor is produced; and

means for igniting said gas-generating composition.

47. A method of inflating an air bag comprising the step of combusting a complex selected from the group consisting of metal nitrite amines, metal nitrate amines, metal perchlorate amines, metal nitrite hydrazines, metal nitrate hydrazines, metal perchlorate hydrazines, and mixtures thereof, wherein a

mixture of gases comprising water vapor and nitrogen gas is produced by the combustion of the complex.

48. A method as defined in claim 47 wherein the combustion of the complex is stoichiometric to metal or metal oxide, nitrogen, and water vapor.

49. A method as defined in claim 47 wherein said mixture of gases comprises water vapor and nitrogen gas.

50. A method as defined in claim 47 wherein the mixture of gases is substantially free of carbon dioxide and carbon monoxide gases.

51. A method as defined in claim 27 wherein said complex is a metal nitrate hydrazine.

52. A method as defined in claim 27 wherein said complex is a metal perchlorate hydrazine.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/00029

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C06B 47/08, 31/00

US CL : 149/36, 45; 280/741; 60/205.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 149/36, 45; 280/741; 60/205.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X -- Y	US, A, 5,266,132 (DANEN ET AL.) 30 NOVEMBER 1993. SEE COL. 5, LINES 35-45.	1-26 ----- 1-50
X -- Y	US, A, 5,160,386 (LUND ET AL.) 03 NOVEMBER 1992, SEE THE ABSTRACT.	1-26 ----- 1-50
X -- Y	US, A, 4,336,085 (WALKER ET AL.) 22 JUNE 1982, SEE COL. 5, LINES 16-20.	1-26 ----- 1-50
X -- Y	US, A, 3,673,015 (SOLLOTT ET AL.) 27 JUNE 1972, SEE THE ABSTRACT AND TABLE I, COL. 2.	1-26 ----- 1-50
A	US, A, 3,463,684 (DEHN) 26 AUGUST 1969, SEE COL. 2,	1-50

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

19 APRIL 1995

Date of mailing of the international search report

22 MAY 1995

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/00029

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,066,139 (ZHIVADINOVICH ET AL.) 27 NOVEMBER 1962, SEE COL. 1, LINES 43-55 AND COL. 3, LINES 5, 15-17, E.G.	1-50
X	US, A, 3,664,898 (TAYLOR ET AL.) 23 MAY 1972, SEE COL. 2, LINES 30-34.	1-26
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Y		1-50
X	US, A 3,977,981 (DUNLOP ET AL.) 31 AUGUST 1976, SEE COL. 4, LINES 1-2.	1-26
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Y		1-50
X	US, A, 4,185,008 (CASPARI ET AL.) 22 JANUARY 1980, SEE COL. 6, LINES 22-36 AND COL. 8, LINES 8-13.	1-26
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Y		1-50
X	INORGANIC CHEMISTRY, VOL. 9, #6, JUNE 1970, HAGEL ET AL., "THE TRIAMMINES OF COBALT(III)...", PP 1496-1502.	1-26
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X	SYNTH. REACT. INORG. MET.-ORG. CHEM., 12(4), (1982), Patil et al., pages 383-394	1-26
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Y		1-50
X	COMPREHENSIVE INORGANIC CHEMISTRY, VOL. 3. BAILAR ET AL. ed., (1973), PAGES 60, 61, 170, 1249, 1250, 1266-69, AND 1366-67.	1-26
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